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(54) **SEPARATION PAR SOLVANT DU BITUME D'UNE MOUSSE DE SABLES BITUMINEUX**

(54) **SOLVENT PROCESS FOR BITUMEN SEPARATION FROM OIL SANDS FROTH**
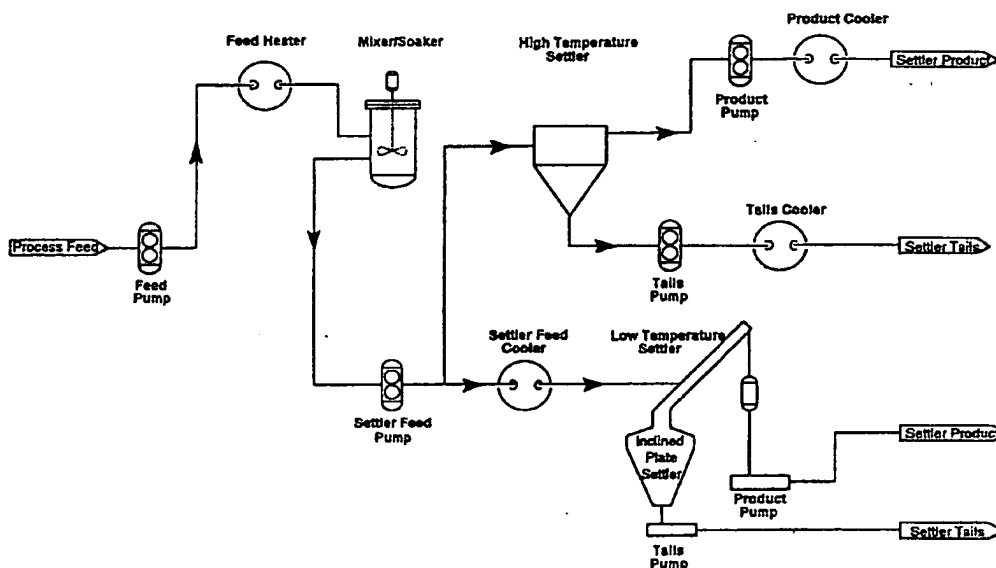
(57) Un solvant paraffinique est mélangé à une mousse de bitume contenant de l'eau et des solides. La quantité de solvant ajoutée est suffisante pour induire l'inversion lorsque le mélange est assujetti à la gravité ou aux forces centrifuges. L'émulsion est transférée dans la phase aqueuse, et on obtient un produit de bitume sec.

(57) A paraffinic solvent is mixed with bitumen froth containing water and solids. Sufficient solvent is added to induce inversion when the mixture is subjected to gravity or centrifugal forces. The emulsion reports to the water phase and a dry bitumen product is obtained.

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1   "SOLVENT PROCESS FOR BITUMEN SEPARATION FROM OIL SANDS FROTH"

2   ABSTRACT OF THE DISCLOSURE

3   A paraffinic solvent is mixed with bitumen froth containing water and

4   solids. Sufficient solvent is added to induce inversion when the mixture is subjected

5   to gravity or centrifugal forces. The emulsion reports to the water phase and a dry

6   bitumen product is obtained.

FIELD OF THE INVENTION

This invention relates to a paraffinic solvent addition method for separating water and solids from bitumen froth.

BACKGROUND OF THE INVENTION

The present invention has been developed in connection with a plant for extracting bitumen from the Athabasca oil sand deposit. At this operation, the oil sands are surface-mined and the contained bitumen is separated from the sand and recovered using what is known as the Clark hot water extraction process ("CHWE"). (The terms "oil" or "bitumen" are used interchangeably herein to identify the hydrocarbon content of oil sand.)

The CHWE process is well known to those in the industry and is described in the patent literature. The "front end" of the process, leading up to the production of cleaned, solvent-diluted bitumen froth, will now be generally described.

The as-mined oil sand is firstly mixed with hot water and caustic in a rotating tumbler to produce a slurry. The slurry is screened, to remove oversize rocks and the like. The screened slurry is diluted with additional hot water and the product is then temporarily retained in a thickener-like vessel, referred to as a primary separation vessel ("PSV"). In the PSV, bitumen globules contact and coat air bubbles which have been entrained in the slurry in the tumbler. The buoyant bitumen-coated bubbles rise through the slurry and form a bitumen froth. The sand in the slurry settles and is discharged from the base of the PSV, together with some water and a small amount of bitumen. This stream is referred to as "PSV underflow". "Middlings", comprising water containing non-buoyant bitumen and fines, collect in the mid-section of the PSV.

1   The froth overflows the lip of the vessel and is recovered in a launder.

2 This froth stream is referred to as "primary" froth. It typically comprises 65 wt. %

3 bitumen, 28 wt. % water and 7 wt. % particulate solids.

4   The PSV underflow is introduced into a deep cone vessel, referred to as

5 the tailings oil recovery vessel ("TORV"). Here the PSV underflow is contacted and

6 mixed with a stream of aerated middlings from the PSV. Again, bitumen and air

7 bubbles contact and unite to form buoyant globules that rise and form a froth. This

8 "secondary" froth overflows the lip of the TORV and is recovered. The secondary froth

9 typically comprises 45 wt. % bitumen, 45 wt. % water and 10 wt. % solids.

10   The middlings from the TORV are withdrawn and processed in a series

11 of sub-aerated, impeller-agitated flotation cells. Secondary froth, typically comprising

12 40 wt. % bitumen, 50 wt. % water and 10 wt. % solids, is produced from these cells.

13   The primary and secondary froth streams are combined to yield a

14 product froth stream, typically comprising 60 wt. % bitumen, 32 wt. % water and 8 wt.

15 % solids. This stream will typically have a temperature of 80°C.

16   The water and solids in the froth are contaminants which need to be

17 reduced in concentration before the froth can be treated in a downstream refinery-type

18 upgrading facility. This cleaning operation is carried out using what is referred to as

19 a "dilution centrifuging circuit".

20   More particularly, the combined froth product is first deaerated and then

21 diluted with sufficient solvent, specifically naphtha, to provide a solvent to froth ("S/F")

22 ratio of about 0.45 (w/w). This is done to increase the density differential between the

23 bitumen on the one hand and the water and solids on the other. The diluted froth is

24 then processed in a scroll-type centrifuge, to remove coarse solids. The bitumen

1 product from the scroll machine is subsequently processed in a disc-type centrifuge,

2 to remove water and fine clay solids.

3 The "cleaned" bitumen product from the dilution centrifuging circuit

4 typically contains 3 to 5 wt. % water and about 0.6 wt. % solids.

5 The underflows from the TORV, the flotation cells and the dilution

6 centrifuging circuit are discharged as tailings into a pond system. Water is recycled

7 from this pond for use as plant process water.

8 There are two significant problems associated with producing a cleaned

9 diluted froth still containing such quantities of water and solids. Firstly, one is

10 precluded from shipping the product through a commercial pipeline that is conveying

11 discrete shipments of a variety of hydrocarbon products. Such pipelines require that

12 any product shipped must contain less than 0.5 wt. % B S and W (bottom settlings

13 and water). Because of this requirement, one must upgrade the cleaned diluted froth

14 produced by the dilution centrifuging circuit in a refinery-type upgrading circuit located

15 close to the mining site, before shipping it. Providing and operating an upgrading

16 circuit at the mine site is very expensive. Secondly, there is a build-up in the

17 concentration of chlorides in plant process water that occurs over time. This build-up

18 arises from recycling water from the tailings pond to the tumbler and re-using the

19 tailings water as part of the water used as process water. In addition, the incoming oil

20 sands contain salt which adds to the chloride content in the process water. Keeping

21 in mind that the cleaned diluted bitumen product from the dilution centrifuging circuit

22 contains a significant fraction of plant water, chlorides are brought by this fraction into

23 the upgrading circuit. These chlorides are harmful in the upgrading circuit, as they

24 cause corrosion and catalyst fouling.

1   The industry has long understood that it would be very desirable to

2 produce a dry diluted bitumen froth product containing less than about 0.5 wt. % water

3 plus solids. Stated alternatively, it would be desirable to separate substantially all of

4 the water and solids from the froth.

5   Many potential solutions have been explored. These have included

6 electrostatic desalting, water-washing, chemicals addition, third stage centrifuging and

7 high temperature froth treatment. However, no effective and practical technique has

8 yet emerged which would produce dry bitumen with little accompanying bitumen loss

9 with the water.

10   There are various reasons why no successful technique has yet been

11 devised for cleaning bitumen froth to reduce the water plus solids content below 0.5

12 wt. %. The major reason is that the water remaining in naphtha-diluted bitumen froth

13 is finely disseminated in the bitumen as globules having a diameter of the order of 3

14 microns or less. The mixture is an emulsion that tenaciously resists breakdown.

15   In this background, only the CHWE process has been mentioned. There

16 are other water extraction processes - such as the known OSLO process, the Bitmin

17 process, and the Kryer process - which also produce bitumen froth which can be

18 cleaned by this invention.

19   With this background in mind, it is the objective of the present invention

20 to provide a new method for cleaning bitumen froth, produced by a water extraction

21 process, which method is effective to better reduce the water plus solids content,

22 preferably to about 0.5 wt. % or less.

SUMMARY OF THE INVENTION

The present invention is directed toward the breaking of the water emulsion in bitumen froth. The invention is based on the discovery that a paraffinic solvent, if added to the bitumen froth in sufficient amount, causes an inversion of the emulsion. That is, the emulsion, a complex mixture of water, bitumen, solvent and solids, which is initially in the hydrocarbon phase, is transferred into the aqueous phase. As a result of the inversion, contained water effectively separates from the diluted froth under the influence of gravity or centrifugal forces. The product is essentially dry diluted bitumen, preferably having a solids and water content less than 0.5 wt. %. (This product is hereafter referred to as dry bitumen.)

It is believed that the water globules agglomerate in the presence of the critical concentration of the paraffinic solvent and acquire the capacity to segregate from the hydrocarbon.

In a preferred embodiment, the invention involves a method for cleaning bitumen froth containing water and particulate solids contaminants, said froth having been produced by a water extraction process practised on oil sands, comprising: adding paraffinic solvent to the froth in sufficient amount to produce a solvent to froth ratio ("S/F") of at least 0.6 (w/w); and subjecting the mixture to gravity or centrifugal separation for sufficient time to reduce its water plus solids content to less than about 0.5 wt %. Most preferably the solvent used is natural gas condensate, a mixture of low molecular weight alkanes with chain lengths from about C_5-C_{16}, added in sufficient amount to produce a solvent to froth ratio of about 1.0 (w/w).

The invention is characterized by the following advantages:

- substantially all of the water can be removed from the froth by diluting it with sufficient paraffinic solvent;

- bitumen losses with the separated water are no worse than the conventional process;

- the asphaltene content in bitumen lost with the water is no higher than that normally associated with bitumen - thus the lost bitumen can be recovered from the water using conventional techniques; and

- the new method has been shown to be effective at relatively low temperatures (40 - 50°C), which raises the possibility that the extraction process can be run at lower temperatures.

The method of this invention involves the mixing of the solvent with the bituminous froth, preferably in a vessel, for a sufficient time to ensure the complete dispersion of the solvent into the froth. Normally, this can be carried out in a stirred tank with a nominal retention time of 5 minutes. The separation itself can be carried out in the same vessel by stopping the agitation and permitting the water droplets to separate under the influence of gravity. In a continuous process, the separation can be conducted in a separate settling vessel which is connected by piping to the mixing vessel.

DESCRIPTION OF THE DRAWINGS

Figure 1 is a plot showing the residual water content remaining in the oil phase over time in a gravity settling test where the bitumen froth has been diluted with various solvents at conditions which are conventional: 80°C, S/F ratio 0.45 w/w. The Plant 7 naphtha represents the conventional solvent used in the commercial plant owned by the present assignees;

1   Figure 2 is a plot similar to Figure 1, showing the residual water content

2   remaining in the oil phase over time in a gravity settling test for runs conducted at the

3   same conditions as those of Figure 1, except that the S/F ratio was increased to 0.91 -

4   of significance is the elimination of water from the oil phase at this S/F ratio;

5   Figure 3 is a plot showing the residual water content remaining in the oil

6   phase after 30 minutes of settling time for runs using heptane as the solvent at

7   different S/F ratios. Conditions: centrifuging at 2000 rpm for 10 mins., 80°C - the

8   results indicate that inversion occurred at a S/F ratio of about 0.75 - 0.80;

9   Figure 4 is a plot showing the residual water content remaining in the oil

10   phase over time in a gravity settling test using: (a) natural gas condensate ("NGC")

11   as the solvent for runs at different S/F ratios, and (b) the results of a single run using

12   Plant 7 naphtha as the solvent at a high S/F ratio - of significance is the inversion for

13   NGC at an S/F ratio of about 1.00 to 1.20.

DESCRIPTION OF THE PREFERRED EMBODIMENT

15   A comparative testing program was undertaken under laboratory

16   conditions. Different solvents were added to bitumen froth as diluents. The solvents

17   varied in aromatic and paraffin contents. Various solvent/froth ratios were tried for

18   each diluent. Various temperatures were tried. After adding the solvent, the diluted

19   froth was centrifuged or gravity settled and the residual water, chloride and solids

20   contents in the bitumen fraction were determined. The resulting data were then

21   assessed.

22   In the course of the testing, certain discoveries were made, as described

23   below. The inventive process is based on these discoveries.

1   More particularly, the test program involved the following materials and

2   procedures:

3   A single froth was used for all of the test runs. This froth assayed as

4   follows:

5   oil (or bitumen) - 66.22 wt. %

6   water - 24.59 wt. %

7   solids - 9.65 wt. %

8   The solvents used in the test are set forth in Table 1.

Table 1

Solvents Used For Water Removal Studies From Froth

	Class.**	Solvent	Source	Aromatics Content (%)	b.p. (°C)	Density (g/ml)
1						
2						
3						
4	A	Pt. 7 Naphtha	SCL Pt. 7	~15%	82 ~ 171	0.770
5	A	Aromatic naphtha	Esso	~98%	143 ~ 186	0.872
6	A	Toluene	Fisher Sci.	100%	111	0.866
7	A	Xylene	Fisher Sci.	100%	139	0.868
8	P	Hexane	Fisher Sci.	0%	69	0.664
9	P	Heptane	Fisher Sci.	0%	98	0.684
10	P	i-Octane	Fisher Sci.	0%	100	0.688
11	P	Hexadecane	Fisher Sci.	0%	287	0.773
12	P	Bayol 35(Light paraff.oil)*	Fisher Sci.	very low	light	0.780
13		Cyclohexane	Fisher Sci.	0%	81	0.779
14		Cyclohexene	Fisher Sci.	0%	83	0.810
15	*	indicates a trade mark				
16	**	A - designates an "aromatic" or non-paraffinic solvent				
17		P - designates a "paraffinic" solvent				

1   The solvent used in applicants' commercial operation is referred to as

2   Plant 7 naphtha. This solvent is applied in the plant with a solvent/froth ratio of about

3   0.45. It will be noted that Plant 7 naphtha has an aromatics content of approximately

4   15%.

5   Water contents in solvent-diluted bitumen and settled water samples

6   were determined by Karl-Fischer titration.

7   The procedure for the gravity settling runs was as follows, unless

8   otherwise described. Bitumen froth and diluent samples were separately placed into

9   a water bath operated at the temperature desired for the run. Once at temperature,

10   samples of froth and diluent were weighed out, to yield the desired solvent/froth ratio

11   for the run, and combined in a 32 ounce mixing jar. The diluent and froth in the jar

12   were mixed at 500 rpm for 10 minutes using a blade mixer.

13   Upon completion of mixing, the mixture was allowed to stand in the jar

14   in the bath to effect gravity settling.

15   Samples were taken at 0, 5, 15, 30, 60, 90 and 120 minute intervals.

16   The location of the sampling point was about the mid-point of the hydrocarbon fraction.

17   The collected samples were analyzed for water content.

18   Two samples of diluted bitumen product were collected from each run

19   after 120 minutes of settling. One was analyzed for chloride content; the other was

20   analyzed for solids content.

21   The procedure for the centrifuging runs was as follows, unless otherwise

22   described. The bitumen froth and diluent samples were pre-heated to the run

23   temperature in a water bath. Once at temperature, samples of froth and diluent were

24   weighed out, to yield an 80 ml sample having the desired solvent/froth ratio, and

25   transferred into a 125 ml glass jar.

1   The glass jar was placed in a shaker and shaken rigorously for 5

2   minutes, to mix the components.

3   The mixture was then introduced into a 100 ml centrifuge tube and spun

4   at 2000 rpm for 10 minutes.

5   After centrifuging, two diluted bitumen product samples were taken. One

6   sample was analyzed for water content. The other was analyzed for chloride content.

7   Example I

8   In this test, a group of solvents were tested at a S/F ratio of 0.45 (w/w),

9   to assess their capability to remove froth water with gravity settling. The test was run

10   at 80°C. The solvents are described in Table I and identified in Figure 1.

11   As previously stated, the S/F ratio of 0.45 is that used in the commercial

12   plant dilution centrifuging circuit. Plant 7 naphtha is the solvent used in the circuit.

13   The test temperature (80°C) is the same as that used in the plant circuit.

14   The results are tabulated in Table 2 and presented in Figure 1.

15   As shown, the solvents with high aromaticity gave equivalent or better

16   water removal when compared to the paraffinic solvent-heptane, at this S/F ratio.

17   In all of the runs, the residual water content in the diluted bitumen

18   product after 120 minutes of settling was still in excess of 3%.

19   In summary, at the conventional S/F ratio, the aromatic solvents were as

20   good at inducing water separation as the paraffinic solvent; none of the solvents

21   reduced the water content below 3%.

TABLE 2

Residual Water in Hydrocarbon Phase by Gravity Settling at 80°C

Using Different Solvents at S/F Ratio = 0.45

Settling time mins	Heptane	Pt.7 naphtha	Tol/Hep = 1/1	Toluene	Xylene
			Water Content in Oil Phase (%)		
0	15.67	14.81	14.67	14.36	13.50
5	5.93	5.84	5.24	4.95	4.69
15	5.35	5.25	5.14	4.05	4.51
30	5.16	4.93	4.82	4.05	4.23
60	4.48	4.36	4.28	4.08	4.00
90	4.33	4.22	4.15	4.07	3.82
120	4.25	4.11	4.10	3.95	3.69

1   Example II

2   This example reports on a group of runs involving gravity settling and

3   which were carried out at 80°C using various solvents at a relatively high S/F ratio of

4   0.91 (w/w).

5   The results are shown in Table 3 and Figure 2.

TABLE 3

Residual Water in Hydrocarbon Phase by Gravity Settling at 80°C

Using Different Solvents at S/F Ratio = 0.91

Settling time mins	Pt.7 naphtha	Toluene	Aromatic Naphtha	Heptane
	Water Content in Oil Phase (%)			
0	10.89	9.13	9.41	9.32
5	3.74	3.47	2.41	4.28
15	3.44	3.21	2.26	3.78
30	3.02	3.05	2.14	<0.10
60	2.76	2.74	2.09	<0.10
90	2.47	2.47	1.91	<0.10
120	2.27	2.25	1.80	<0.10

1   It will be noted that, at an S/F ratio of 0.91 (w/w), the residual water

2   content in the oil phase was reduced from about 4% (Example I) to about 2 - 2.5% for

3   the aromatic solvents tested.

4   However, the heptane run at the same S/F ratio gave a dramatically

5   different result. After about 15 minutes of settling time, an apparent inversion of the

6   emulsified water was initiated and virtually all of the emulsion settled into the water

7   phase after 30 minutes of settling.

8   Heptane is a paraffinic solvent. These runs disclose the discovery that

9   a paraffinic solvent at a sufficient S/F ratio will remove substantially all of the water

10   from diluted bitumen froth when gravity settled.

11   Example III

12   In this test, runs involving gravity settling were carried out at 80°C using

13   various solvents at increasing S/F ratios.

14   The results are presented in Table 4.

15   It will be noted that for heptane, the residual water content could be

16   reduced to a low value (0.1%) in decreasing settling time as the S/F ratio was

17   increased above about 0.80.

18   The data shows that an inversion can be obtained using heptane when

19   the S/F ratio is at least about 0.80. This inversion is initiated in less time as the ratio

20   is further increased.

21   The Table 4 data further shows that the aromatic solvents (toluene,

22   aromatic naphtha, Plant 7 naphtha) were not capable of producing dry bitumen product

23   at high S/F ratios of 0.91 and 1.35.

TABLE 4

Residual Water in Hydrocarbon Phase by Gravity Settling at 80°C
Using Different Solvents at Different Solvent To Froth Ratios

	Solvent	Heptane	Heptane	Heptane	Heptane	Heptane	Heptane
5	Solvent/Froth Ratio (w/w)	0.70	0.75	0.80	0.91	1.35	1.35
6				Water Content in Oil Phase (%)			
7	Settling time (min) 0	11.88	11.45	11.36	9.32	9.29	8.81
8	5	4.64	4.44	4.24	4.28	4.23	2.28
9	15	4.13	1.48	2.96	3.78	3.82	<0.1
10	30	3.66	1.04	0.31	<0.1	<0.1	<0.1
11	60	3.36	0.56	0.11	<0.1	<0.1	<0.1
12	90	3.08	0.26	0.13	<0.1	<0.1	<0.1
13	120	2.71	0.13	<0.1	<0.1	<0.1	<0.1

	Solvent	Toluene	Toluene	Aromatic Naphtha	Plant 7 Naphtha	Plant 7 Naphtha
16	Solvent/Froth (w/w)	0.91	1.35	0.91	0.91	1.35

17

TABLE 4 (Continued)

Solvent	Toluene	Toluene	Aromatic Naphtha	Plant 7 Naphtha	Plant 7 Naphtha
		Water Content in Oil Phase (%)			
Settling time (min)					
0	9.13	8.20	9.41	10.89	8.03
5	3.47	2.74	2.41	3.74	2.71
15	3.21	2.46	2.26	3.44	2.40
30	3.05	2.25	2.14	3.02	2.08
60	2.74	2.03	2.09	2.76	1.71
90	2.47	1.65	1.91	2.47	1.47
120	2.25	1.44	1.8	2.27	1.22

18

Example IV

1

2   This example reports on runs involving centrifugation separation and use

3   of hexane as the solvent. The results are presented in Table 5. The runs were

4   conducted at temperatures ranging from 30°C to 60°C with increasing S/F ratios. The

5   other runs were conducted at varying temperatures with a constant S/F ratio.

6   The results indicate that inversion occurs for hexane at 60°C at a S/F

7   ratio of about 0.6. It further suggests that the S/F ratio required for inversion

8   diminishes with a lighter solvent.

9   The results further indicate that the invention is operative at temperatures

10   which are low (e.g. 40°C) relative to conventional temperatures (80°C) for dilution

11   centrifuging.

TABLE 5

Residual Water, Chloride and Solids In Hydrocarbon Phase

After Centrifuging Using Hexane as Solvent at Different Temperatures

Solvent	S/F (w/w)	Mixing temp. (°C)	Cent. temp. (°C)	Water (%)	Chloride (ppm)
Hexane	0.50	60	60	2.95	24.0
Hexane	0.55	60	60	2.47	10.1
Hexane	0.60	60	60	<0.1	<1
Hexane	0.70	60	60	<0.1	<1
Hexane	0.80	60	60	<0.1	<1
Hexane	1.00	60	60	<0.1	2.2
Hexane	0.70	50	50	<0.1	<1
Hexane	0.70	40	40	<0.1	<1
Hexane	0.70	30	30	0.76	3.8
Hexane	0.70	60	30	<0.1	

Example V

Table 6 illustrates the effect of temperature on water removal. Hexane was used as a diluent at a hexane/froth ratio of 0.7 w/w and the hydrocarbon samples were centrifuged at 2000 rpm for 10 minutes at temperatures different from the mixing temperature. The data illustrate that separation of the water from the hydrocarbon can be achieved at temperatures above about 30°C.

TABLE 6

Effect of Mixing Temperature and Centrifuging Temperature on

Separation of Water from Hexane Diluted Froth

Hexane/Froth Ratio = 0.7 w/w, Centrifuging 10 mins. at 2000 rpm

Ratio: Mixing Temp °C/ Centrifuging Temp. °C (M°C/C°C)	M30/C30	M60/C30	M40/C40	M50/C50	M60/C60
Water Content in Hydrocarbon, wt. %	0.76	<0.10	<0.10	<0.10	<0.10

Example VI

Table 7 illustrates the solids content for the runs of Figure 2 resulting from the use of heptane solvent at 0.91 solvent/froth ratio, and residual solids contents for hydrocarbons where toluene and Plant 7 naphtha were used as diluents.

TABLE 7

Effect of Diluent Type on Solids Removal from Froth

Settling Temperature 80°C, S/F Ratio = 0.91

Diluent Type	Heptane	Toluene	Plant 7 Naphtha
Solids Residue in Hydrocarbon, wt. %	0.15	0.75	0.79

1   <u>Example VII</u>

2   This example reports on runs involving centrifugation separation and use

3   of paraffinic, cycloparaffinic and olefinic solvents at varying temperatures and a S/F

4   ratio of 1.00 w/w.

5   Table 8 illustrates the effect of cycloparaffinic (cyclohexane) and olefinic

6   (cyclohexene) solvents on water removal at solvent/froth ratios of 1.0 w/w. It is clearly

7   shown that non-paraffinic solvents do not achieve the water removal of paraffinic

8   solvents.

TABLE 8

Residual Water and Chloride in Bituminous Froth Diluted with Various Hydrocarbon Solvents, After Centrifuging

Solvent	Paraffinic Content	b.p.(°C)	Density (g/ml)	S/F (w/w)	Mixing Temp. (°C)	Cent. Temp. (°C)	Water (%)	Chloride (ppm)
Hexane	100%	69	0.664	1.00	60	60	<0.1	2.2
Heptane	100%	98	0.648	1.00	80	80	<0.1	<1
i-Octane	100%	100	0.688	1.00	80	80	<0.1	<1
Hexadecane	100%	287	0.773	1.00	80	80	<0.1	<1
Bayol 35*	98+%		0.780	1.00	80	80	<0.1	<1
Cyclohexane	0%	81	0.779	1.00	80	80	2.04	16.5
Cyclohexene	0%	83	0.810	1.00	80	80	2.36	19.0

* Trade Mark

Bayol 35 is a blend of higher molecular weight paraffins (C_{12+})

1   As shown:

2   •   The paraffinic solvents (hexane, heptane, i-octane, hexadecane

3   and Bayol 35) were all successful in producing dry (0.1%) diluted

4   bitumen product. This group of paraffinic solvents included

5   normal paraffins, isoparaffins (i-octane) and paraffin blends (Bayol

6   35);

7   •   The cycloparaffinic and olefinic solvents were not successful in

8   producing a dry diluted bitumen product;

9   •   Residual chlorides in the hydrocarbon phase were less than 1

10   ppm when paraffinic solvents were used. Cycloparaffinic and

11   olefinic solvents yielded higher chloride contents in the

12   hydrocarbon, which were consistent with retention of salt in the

13   residual water.

14   The term "paraffinic solvent" is used in the claims. This term is intended

15   to cover solvents containing normal paraffins, isoparaffins and blends

16   thereof in amounts greater than 50 wt. %. It is not intended to include

17   olefins, naphthas or cycloparaffins.

18   Example VIII

19   It has long been recognized that asphaltenes will precipitate in pentane.

20   It was reported by Reichert, C., Fuhr, B. J., and Klein, L. L., in "Measurement of

21   asphaltene flocculation in bitumen solutions", J. Can. Pet. Tech. 25(5), 33, 1986, that

22   the onset of asphaltene precipitation in pentane occurs when 1.92 ml/g of pentane is

23   added to Athabasca bitumen. Considering the bitumen content (66.22%) in the tested

froth sample, the asphaltene precipitation threshold is equivalent to 1.27 ml/g of pentane for the froth sample.

As previously established, the minimum solvent to froth ratios for hexane diluent and heptane diluent for water elimination are about 0.60 g/g and 0.80 g/g of solvent based on froth, respectively. By considering the densities of the diluents, these ratios are converted to 0.90 ml/g for hexane and 1.17 ml/g for heptane diluents. Since asphaltene solubility in hexane and heptane is higher than in pentane, it appears that asphaltene precipitation should not be significant in hexane or heptane at S/F ratios close to the inversion point.

To further demonstrate that inversion of the emulsion and not asphaltene precipitation was taking place, a test was conducted where heptane was added to bitumen in different amounts and the quantities of asphaltene precipitating from the solution was observed. The results are reported in Table 9 and clearly show that asphaltenes begin to precipitate from solution at ratios in excess of approximately 1.0 w/w heptane to froth, which exceeds the inversion value of 0.8 w/w heptane to froth as obtained from Figure 3.

TABLE 9

Asphaltene Precipitation Observations with Heptane Diluent

Heptane to bitumen ratio (w/w)	0.68	1.06	1.21	1.37	1.50	1.60	2.04 5.00
Equivalent heptane to froth ratio (w/w)	0.45	0.70	0.80	0.91	1.00	1.06	1.35 3.11
Asphaltene precipitation at room temp.	No	No	No	No	No	little	some lots
Asphaltene precipitation at 80°C	No	No	No	No	No	little	some lots

1   This point is significant for the following reason. There is a hydrocarbon

2   loss with the water fraction. If this loss is asphaltenes, then there is no practical way

3   known to applicants for recovering these lost hydrocarbons.

4   In conclusion, the foregoing examples support:

5   (1)   That paraffinic solvents when used as diluents for froth treatment

6   at appropriate S/F ratios will eliminate substantially all of the

7   water and chloride from froth upon separation using centrifugation

8   or gravity settling;

9   (2)   Both normal and iso paraffinic solvents are efficient in generating

10   dry diluted bitumen products;

11   (3)   Sufficient paraffinic solvent to achieve inversion is needed to

12   produce dry bitumen product - the critical S/F ratio will vary

13   somewhat with the solvent used;

14   (4)   The process works at low and high temperatures; and

15   (5)   Asphaltene precipitation does not appear to be a problem.

16   Example IX

17   A typical commercial solvent, which is largely paraffinic and commonly

18   consists of C_4 - C_{20} hydrocarbons, is natural gas condensate ("NGL"). The composition

19   of this solvent is compared with the Plant 7 naphtha in Table 10, in which the

20   composition is described by various hydrocarbon classes.

26

1

<u>TABLE 10</u>

2 Typical Hydrocarbon Class Compositions of

3 Natural Gas Condensate and Plant 7 Naphtha

4

Component	Paraffins	Naphthenes	Aromatics
Naphtha	43%	40%	17%
Natural Gas Condensate	83%	12%	5%

9   Table 11 and Figure 4 illustrate water removal at different solvent/froth

10 ratios using natural gas condensate as a solvent. In this example, water and solids

11 were eliminated from the hydrocarbon at solvent/froth ratios exceeding 1.0 w/w.

TABLE 11

Water Removal Results From Froth With

Natural Gas Condensate As Diluent By Gravity Settling at 40°C

Solvent		NGC	NGC	NGC	Pt.7 Naphtha
Solvent/Froth Ratio (w/w)		0.80	1.00	1.20	1.35
Temperature (°C)		40	40	40	80
Water Content In Oil Phase (%)					
Settling time (min)	0	8.83	8.16	7.58	8.03
	5	7.32	6.79	6.22	2.71
	15	6.01	2.8	<0.1	2.4
	30	1.75	<0.1	<0.1	2.08
	45	1.72	<0.1	<0.1	
	60	1.62	<0.1	<0.1	1.71
	90				1.47
	120				1.22

As shown, runs were carried out using S/F ratios of 0.80, 1.00, and 1.20. On the run having a S/F ratio of 1.00, the water removal increased dramatically (relative to S/F ratio = 0.80 run) and dry bitumen was produced. Stated otherwise, inversion was obtained using NGC at S/F ratio of 1.00 (w/w).

By comparison, a run using Plant 7 naphtha at 80°C and S/F ratio of 1.35 was unsuccessful in producing dry bitumen.

As stated, using NGC as the diluent at S/F ratios of 1.00 or greater resulted in substantially all of the water being removed from the oil. However a brownish rag layer was produced between the oil and water layers. See Figure 4 and Table 12.

TABLE 12

Rag Layers Produced During Gravity Settling with

Natural Gas Condensate as Froth Diluent

Settling time (min)	Rag layer/(rag layer + upper oil layer); Vol %	
	NGC/Froth = 1.00(w/w)	NGC/Froth = 1.20(w/w)
30	30%	25%
60	23%	17%
90	22%	15%
120	18%	13%
3 days	9%	8%
Composition of rag after 120 min settling	51.97% + 48.03% water plus solids	/

As settling was extended, the volume of the rag layer diminished. After settling for 120 minutes, the composition of the rag layer reached about 50% oil and 50% water plus solids.

When the rag layer was separated from the other layers and centrifuged at 2000 rpm for 10 minutes, the water and hydrocarbon separated, leaving oil containing less than 0.1% water.

1 Example X

2   This example reports on a run conducted in a scaled up pilot circuit using

3 NGC as the diluent. The run was operated at 50°C and then the temperature was

4 increased over time, reaching 127°C. The S/F ratio was maintained at about

5 1.20(w/w).

6   The pilot unit used is outlined schematically in Figure 5.

7   The results are set forth in Table 13.

8   The pilot unit consisted of a feed system where froth and diluent were

9 pumped through a heater and into a mixing vessel which had a nominal retention time

10 of 2 - 5 minutes. Pressures in the system were held at approximately 1000 Kpa.

11 Product from the mixer was passed under pressure into the settling vessel which had

12 a nominal 15 minutes residence time. The oil/water interface was monitored and

13 controlled by a conductivity probe. The products, both hydrocarbon and slurry

14 underflow, were discharged from the process through coolers and then the pressure

15 released through positive displacement pumps.

16   The run continued for a period of 7-1/4 hours with approximately one-half

17 of the operating time at 50°C and the other half at 117°C (ave).

18   The results show that dry diluted bitumen could be recovered when the

19 process was operated at both temperatures. (See Table 13.)

TABLE 13

Froth Treatment Pilot Test Results with Natural Gas Condensate as Froth Diluent

	Froth Flow Kg/min	Condensate Flow kg/min	Diluent Froth Flow kg/min	Settler Product kg/min	Settler Tails kg/min
Run #1	0.823	0.881	1.704	1.10	0.60
Rune #2	0.823	0.966	1.788	1.39	0.40

	Temperature Deg C	Mixing Speed	Pressure Kpa	Hydrocarbon Recovery (%)	Product Quality (%HC)	Chloride Removal (%) Wt. %	Hydrocarbon Solids Content
Run #1	49	500	1000	83.8	99.2	98	0.06
Run #2	117	500	1000	97.6	90.7	77	0.32

31

TABLE 14

Centrifuging Results of Underflows From Pilot Runs

Underflow Sample	From 50°C pilot run; Natural gas condensate	From 120°C pilot run; Natural gas condensate	From 120°C pilot run; Plant 7 naphtha
Density of U/F before cent.	0.92g/ml	0.98g/ml	
Upper oil after centrifuging	33.8%	11.8%	9.0%
Rag after centrifuging	41.2%	3.4%	none
Water after centrifuging	14.7%	58.9%	71.3%
Bottom solids after cent.	10.3%	25.9%	19.7%
Water % in rag from cent.	73.8%	50.5%	/
Water % in recovered oil by cent.	<0.1%	<0.1%	0.35%

However, it was found that, at the low operating temperature (50°C), oil losses with the water and solids underflow were relatively high. At the high operating temperature (~120°C), the oil losses with the underflow were minimal. More particularly, samples of the underflow were centrifuged in a laboratory centrifuge at 2000 rpm for 10 minutes. The centrifuge contents separated into 4 layers, specifically: a clean oil layer; a viscous rag layer; a water layer; and a solids layer. The relative proportions are stated in Table 14. Most of the solids in the hydrocarbon were also removed.

1   In conclusion, the results teach that NGC can successfully be used as

2   the diluent at low and high temperatures to yield dry diluted bitumen. However, the low

3   temperature process produces relatively low quality underflow and the underflow has

4   a relatively high rag content.

1 THE EMBODIMENTS OF THE INVENTION IN WHICH AN

2 EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS

3 FOLLOWS:

4

5   1. A method for cleaning bitumen froth containing water and

6 particulate solids contaminants, said froth having been produced by a water

7 extraction process practised on oil sand, comprising:

8   adding a sufficient amount of paraffinic solvent to the froth to induce

9 inversion;

10   mixing the froth and the solvent for a sufficient time to disperse the

11 solvent in the froth; and

12   subjecting the mixture to gravity or centrifugal separation for a

13 sufficient period to separate substantially all of the water and solids from the

14 bitumen to produce dry diluted bitumen.

15

16   2. A method for cleaning bitumen froth containing water and

17 particulate solids contaminants, said froth having been produced by a water

18 extraction process practised on oil sand, comprising:

19   adding paraffinic solvent to the froth in sufficient amount to produce a

20 solvent to froth ratio of at least about 0.6 (w/w) to induce inversion;

21   mixing the froth and the solvent for a sufficient time to disperse the

22 solvent in the froth; and

23   subjecting the mixture to gravity or centrifugal separation for sufficient

24 time to reduce its water plus solids content to less than about 0.5 weight percent.

3. The method as set forth in claim 2 wherein the froth was produced by the Clark hot water extraction process.

4. The method as set forth in claim 2 or 3 wherein the solvent is natural gas condensate containing more than 50% paraffins.

5. The method as set forth in claim 2 or 3 wherein the solvent is natural gas condensate containing more than 50% paraffins and added in sufficient amount to produce a solvent to froth ratio of at least 1.00 (w/w).

6. The method as set forth in claim 2 or claim 3, wherein the solvent is natural gas condensate containing more than 50% paraffins and added in sufficient amount to produce a solvent to froth ratio of greater than about 0.8 (w/w).

Fig.1 Solvent Effect on Water Removal;
80°C Gravity Settling; S/F = 0.45(w/w)

Fig.1 Solvent Effect on Water Removal; 80°C Gravity Settling; S/F = 0.45(w/w)

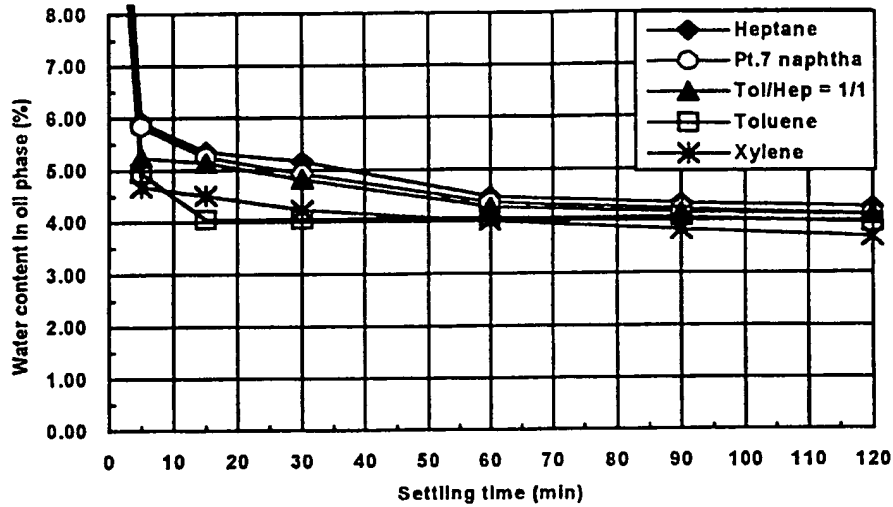## Fig. 2: Solvent Effect on Water Removal; 80oC Gravity
Settling; S/F Ratios = 0.91
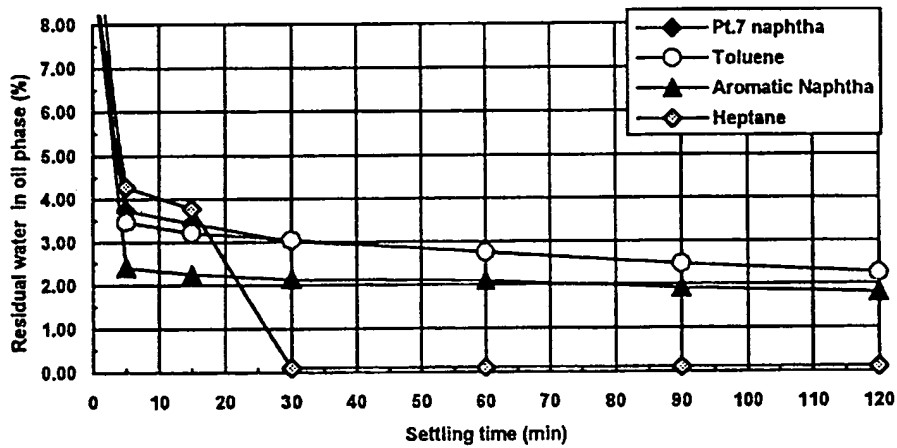

Fig. 2: Solvent Effect on Water Removal; 80oC Gravity Settling; S/F Ratios = 0.91

Fig. 3: Solvent/Froth Ratio Effect on Water Removal; Heptane
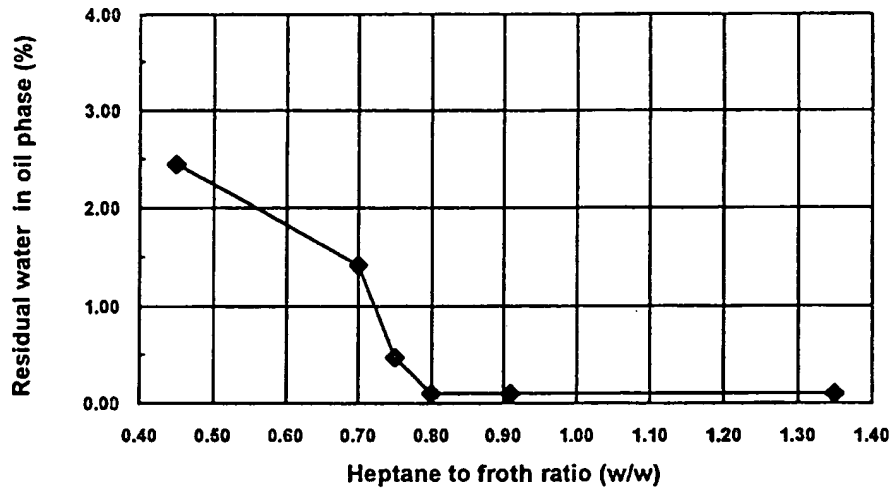as Diluent; Centrifuging, 2000 rpm, 10 min, 80oC

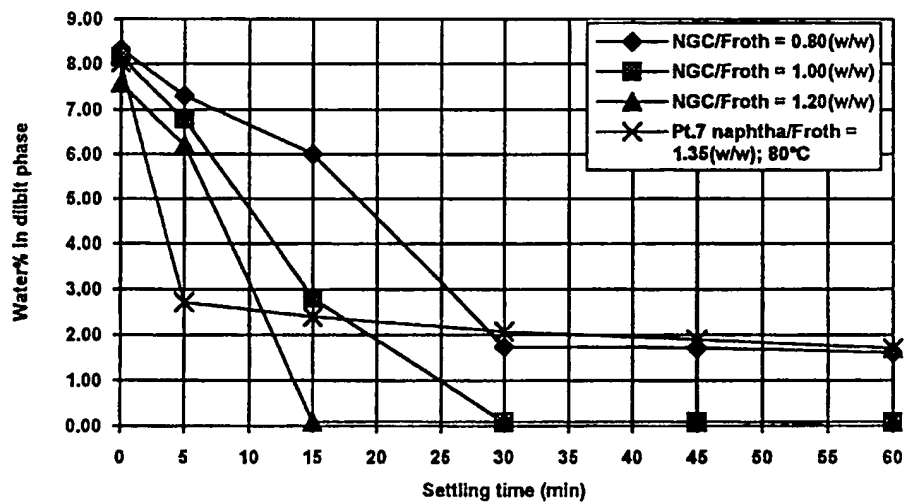Fig.4 Water Rem'l at Diff. S/F Ratios; 40°C gravity Settling; NG
Condensate

Fig.5 Pilot Plant Flow Diagram

Feed Heater Mixer/Soaker High Temperature Settler Product Cooler

Settler Product

Product Pump

Process Feed

Feed Pump

Tails Cooler

Settler Tails

Tails Pump

Settler Feed Cooler Low Temperature Settler

Settler Feed Pump

Inclined Plate Settler

Settler Product

Product Pump

Settler Tails

Tails Pump